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PAPER PRODUCT IMPREGNATED WITH CHEMICAL MATERIAL

RELATED APPLICATION

[0001] This application is a continuation of U.S. Patent Application Serial No. 09/302,937, filed April 30, 1999.

FIELD OF THE INVENTION

[0002] The present invention relates to a paper product impregnated with chemical material to accomplish a variety of industrial and household tasks.

DESCRIPTION OF THE RELATED ART

[0003] Paper is typically formed from a mesh of fine fibers, generally of vegetable origin. Currently, wood pulp is the most common source for paper. However, other fibrous material such as cotton, flax, kenaf, hemp, or straw have been used in paper manufacture. Most commonly paper is produced in the form of thin sheets. However paper can also be manufactured in other physical forms such as compressed pellets.

[0004] Paper products currently enjoy widespread use in almost every field of human endeavor. Paper is used as sterile packaging for surgical instruments, and as a cheap, disposable covering for surfaces in treatment and operating rooms. In the food service industry, paper is universally utilized to store both solid and liquid foods, as well as to serve those foods to the consumer. Paper is also emerging as a major component in absorbent material for disposal of wastes from pets and other sources, for example in the material known as cat litter.

[0005] Given the wide uses for paper products, there is a need in the art for a paper product which receives, retains, and releases useful chemical species.

[0006] Unfortunately, paper provides a suitable environment for the growth of microorganisms. The ability of paper to support the growth of bacteria, molds, or fungi is attributable to the fact that paper is itself is derived from living tissue and contains residual organic material that can provide sustenance for microorganisms.

[0007] The unwanted growth of microorganisms poses a health hazard for many of the potential applications for paper products. For example, maintaining a sterile environment during the treatment of illness and injury has proven to dramatically reduce the possibility of infection. In the area of food services, maintaining an micro-organism free environment prolongs the viability of foodstuffs, and enhances the effect of such processes as pasteurization. In waste disposal applications, reduction in the growth of microorganisms can cut down on noxious odors and the danger of infection to waste-handlers.

[0008] Therefore, there is also a need in the art for a paper product which can inhibit the growth of microorganisms, and which is cheap and easy to manufacture.

SUMMARY OF THE INVENTION

[0009] The present invention relates to a porous paper material which has been impregnated with at least one chemical material. The impregnating chemical may beneficially react with other chemicals.

[0010] In one embodiment, paper is impregnated with hydrogen peroxide and acetic acid, and reaction between the hydrogen peroxide and acetic acid creates peracetic acid. Peracetic acid is both biocidal and volatile. The gaseous peracetic acid diffuses out of pores in the paper, creating a no-growth zone on the surface of and immediately surrounding the paper. In this manner, chemically impregnated paper in accordance with the present invention may promote a sterile environment useful for a wide variety of activities, for example in the treatment of illness/injury, or in the packaging/storage of foodstuffs.

[0011] A method for sterilizing an area in accordance with the present invention comprises the steps of impregnating a porous paper product with a chemical material, placing the porous paper product in the area, and causing reaction of the impregnated chemical material to produce a biocidal compound.

[0012] A method for impregnating a porous paper product in accordance with one embodiment of the present invention comprises the steps of providing the porous paper product having pores and a surface, and exposing the surface of the porous paper product to at least one chemical which conveys biocidal properties to the porous paper product.

[0013] A composition for producing peracetic acid in accordance with one embodiment of the present invention comprises a porous paper product impregnated with hydrogen peroxide and an acid.

[0014] The features and advantages of the present invention will be understood upon consideration of the following detailed description of the invention and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

[0015] FIG. 1 illustrates a method for creating a sterile field utilizing chemically impregnated sheets of paper in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION

[0016] The present invention relates to a paper product that has been impregnated with at least one chemical reaction and/or diffusion of this chemical out of the pores of the paper gives rise to

a number of beneficial properties. In particular, diffusion of an impregnating volatile antimicrobial or biocidal agent creates a sterile environment at the surface and in the immediate vicinity of the paper.

[0017] Paper is a highly porous material. These pores are defined by space between the extremely fine vegetable fibers making up the mesh. The pores in the paper can receive and contain a wide variety of chemical materials.

[0018] For example, the pores in paper can be impregnated with precursors of chlorine dioxide (ClO_2), a gas useful for killing biological contaminants (such as microorganisms, mold, fungi, yeast and bacteria). The biocidal nature of ClO_2 is attributable to its high oxidation potential.

[0019] Chlorine dioxide can be produced in many ways. For example, it is known to generate chlorine dioxide by adding an acid to a metal chlorite solution. Chlorine dioxide can also be generated by adding water to a powdered composition such as ferric sulfate or ferric chloride (or other dry composition). An activated dry composition which absorbs water from the air and releases chlorine dioxide over time may also be prepared.

[0020] In a first class of embodiments of the present invention, a sheet of paper is successively impregnated with sodium chlorite and acetic acid, or one sheet of paper impregnated with sodium chlorite is placed into contact with another sheet of paper impregnated with acetic acid. Mixing by co-diffusion of the two chemicals causes in the following reaction:

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{sodium chlorite}}{NaClO_2} \rightarrow \underset{\text{chlorine dioxide}}{ClO_2}$$

The volatile chlorine dioxide then diffuses from pores of the paper into the surrounding environment. The chlorine dioxide suppresses growth of bacteria, molds, or fungi on the surface of the paper or in areas immediately surrounding the paper.

[0021] Acetic acid is only one acid that can generate chlorine dioxide in accordance with the present invention. Sulfuric acid, phosphoric acid, and propionic acid can also react with sodium chlorite to produce chlorine dioxide. Moreover, these acids can also react with paper impregnated with sodium chlorate to produce chlorine dioxide.

[0022] FIG. 1 illustrates one embodiment of the present invention, wherein separate sheets of paper 10A and 10B are impregnated with sodium chlorite X and acetic acid Y, respectively. Impregnated papers 10A and 10B are separately stored and transported to the site of use, such as a hospital operating room. At the point of use, impregnated papers 10A and 10B are placed in physical contact. Co-diffusion of the sodium chlorite X and acetic acid Y promotes reaction between these chemicals, forming volatile chlorine dioxide Z. Chlorine dioxide Z outgasses from combined papers 10C, inhibiting the growth of microorganisms on the surface of the combined papers 10C as well as in

immediate vicinity 10D of combined papers 10C. This outgassing provides a sterile environment for surgical instrument 12.

[0023] In another embodiment of the present invention, a porous paper product in the form of pellets is impregnated with sodium chlorite and acetic acid. Alternatively, a first bed of paper pellets is impregnated with sodium chlorite, and a second bed of paper pellets is impregnated with acetic acid. Mixing together of pellets from the two beds can promote the formation of chlorine dioxide.

[0024] In a further alternative embodiment of the present invention, a porous paper product in the form of sheets or pellets is successively impregnated with hydrogen peroxide and an acid. Mixing by co-diffusion of the two impregnating compounds produces a peracid. Acids which may be mixed with hydrogen peroxide to produce the corresponding peracid include but are not limited to: acetic acid; propionic acid; citric acid; benezoic acid; phosphoric acid; lactic acid; butyric acid; pentenoic acid; succinic acid; glutaric acid; sorbic acid; and glycolic acid.

[0025] The following chemical reaction shows the specific reaction between acetic acid and hydrogen peroxide to produce peracetic acid:

$$\underset{\text{hydrogen peroxide}}{H_2O_2} + \underset{\text{acetic acid}}{\underset{\overset{\|}{O}}{CH_3COH}} \rightleftharpoons \underset{\text{peracetic acid}}{\underset{\overset{\|}{O}}{CH_3COOH}} + H_2O$$

[0026] Like chlorine dioxide, peracetic acid is a volatile gas having a high oxidation potential and corresponding biocidal properties. Diffusing peracetic acid creates the same type of sterile field discussed above in connection with chlorine dioxide.

[0027] A variety of methods may be utilized to impregnate the paper with chemical materials. For example, the paper may be dunked or immersed in a bath containing the chemical, with the liquid chemical drawn into the pores of the paper through the process of diffusion. Alternatively, the chemical may be sprayed upon the surface of the paper, with impregnation of the paper accomplished through diffusion of the chemical from the paper's surface into the underlying pores.

[0028] The present invention is applicable to impregnate a variety of porous paper products. Paper made from softwood pulp, kenaf, flax, and hemp are all suitable for chemical impregnation in accordance with the present invention.

[0029] In order to further illustrate the present invention, the following experimental examples are described. Each of these examples illustrates impregnation of paper with chemicals that impart biocidal properties.

Example Number 1

[0030] The antimicrobial properties of a number of samples of impregnated kenaf papers was determined by exposing *E. coli* bacteria during its growth period to the impregnated paper. This was done by using a zone of inhibition test.

[0031] A half inch square of the impregnated sample kenaf paper was placed in the center of a Petri dish containing an agar and *E. coli* bacteria spread on the agar surface. Where *E. coli* bacteria were unable to multiply to form visible colonies due to the effects of the test paper, the agar media remained clear. This clear area is known as the zone of inhibition. Bacteria outside of this zone of inhibition are not affected by their proximity to the sample and grow to form visible colonies.

[0032] A number of samples were prepared according to TABLE 1:

TABLE 1

Sample Number	Sample Components (all % by weight)
1	35% aqueous hydrogen peroxide 99% acetic acid
2	paper only - no impregnated chemicals
3	5% limonene in water
4	5% limonene in water 35% aqueous hydrogen peroxide
5	50% aqueous potassium sorbate 99% acetic acid
6	50% aqueous potassium sorbate 5% limonene in water
7	50% aqueous potassium sorbate 35% aqueous hydrogen peroxide

The chemicals to be impregnated in each sample were sprayed onto sheets of kenaf paper in equal parts of 2 cc/ft^2 of paper surface area. The paper was allowed to dry, and a 1/2" x 1/2" square of the impregnated paper was cut to serve as a sample.

[0033] A petri dish with Standard Plate Count Agar was inoculated with *E. coli* bacteria by using a bottle with 99 ml sterile phosphate-buffered dilution water, to which is added one loopful of diluted *E. coli* culture. A sterile cotton swab was dipped into the dilution water -containing the *E. coli* culture, then the swab was liberally wiped over the entire surface of the agar. After this, the 1/2 inch square of the paper sample was placed in the middle of the dish, and the dish was then sealed. After

two days growth at 35°C, the zone of inhibition around the paper was measured from all four sides and averaged.

[0034] The results of the zone of inhibition test for *E. coli* bacteria for the samples listed in TABLE 1 are shown in TABLE 2:

TABLE 2

Zone of Inhibition Test Using *E. Coli* Bacteria

Sample #	Side #1	Side #2	Side #3	Side #4	Avg. Length
1	2.6 cm	2.7 cm	2.6 cm	2.6 cm	2.63 cm
2	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm
3	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm
4	2.9 cm	2.8 cm	3.0 cm	2.7 cm	2.85 cm
5	1.3 cm	1.0 cm	1.0 cm	1.1 cm	1.1 cm
6	1.0 cm	1.1 cm	1.0 cm	1.0 cm	1.03 cm
7	0.5 cm	0.6 cm	0.5 cm	0.5 cm	0.53 cm

[0035] Review of TABLE 2 indicates that sample no. 4 (5% limonene/35% aqueous hydrogen peroxide) was most effective in inhibiting the growth of the E. Coli bacteria. Sample no. 1 (99% acetic acid/35% aqueous hydrogen peroxide) was the next most effective mixture. Neither the control (sample no. 2) nor limonene alone (sample no. 3) showed any effectiveness against the E. Coli bacteria.

Example Number 2

[0036] A second zone of inhibition test was next performed to test the ability of the samples of TABLE 1 to inhibit growth of the *Penicillium* mold.

[0037] A Petri dish with Standard Plate Count Agar was inoculated with a wild strain of the *Penicillium* mold by using a bottle with 99 ml sterile phosphate-buffered dilution water, to which was added a moistened cotton swab that has been rubbed on the top of a growing colony of *Penicillium*. A new sterile cotton swab was dipped into the dilution water containing the *Penicillium* culture, then the swab was liberally wiped over the entire surface of the agar. After this, a 1/2 inch square of the paper sample was placed in the middle of the dish, and the dish was then sealed.

[0038] After four days growth at room temperature, the zone of inhibition was measured from all four sides and averaged. The results are shown in TABLE 3:

TABLE 3

Zone of Inhibition Test Using
Wild Strain of *Penicillium* Mold

Sample #	Side #1	Side #2	Side #3	Side #4	Avg. Length
1	1.8 cm	1.7 cm	1.8 cm	1.9 cm	1.8 cm
2	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm
3	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm
4	2.3 cm	2.2 cm	2.3 cm	2.2 cm	2.25 cm
5	1.1 cm	1.0 cm	1.0 cm	1.0 cm	1.02 cm
6	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm
7	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm

[0039] Review of TABLE 3 indicates that sample no. 4 (5% limonene/35% aqueous hydrogen peroxide) was again most effective at inhibiting the growth of microorganisms. Sample no. 1 (99% acetic acid/35% aqueous hydrogen peroxide) was again the next most effective mixture. Neither the control (sample no. 2) nor limonene alone (sample no. 3) showed any effectiveness against the Penicillium mold.

Example Number 3

[0040] To evaluate the effect upon biocidal activity of the type of paper impregnated with chemical species, a third zone of inhibition test was conducted. This test utilized a second set of samples prepared according to TABLE 4:

TABLE 4

Sample Number	Paper Type	Sample Components (all % by weight)
8	flax	50% aqueous citric acid 35% aqueous hydrogen peroxide
9	hemp	50% aqueous citric acid 35% aqueous hydrogen peroxide
10	kenaf	50% aqueous citric acid 35% aqueous hydrogen peroxide
11	wood pulp	5% limonene in water 35% aqueous hydrogen peroxide
12	kenaf	100% 50% aqueous citric acid
13	kenaf	100% 35% aqueous hydrogen peroxide

Again, the components of each sample were sprayed onto the paper in equal parts of 2 cc/ft^2 of paper surface area. The paper was allowed to dry, and a 1/2" x 1/2" square of the impregnated paper were then cut to serve as a sample.

[0041] A zone of inhibition test was then performed in the presence of *E. coli* bacteria, as otherwise described above in Example Number 1. The results are shown in TABLE 5:

TABLE 5
Zone of Inhibition Test Using *E. Coli* Bacteria

Sample #	Side #1	Side #2	Side #3	Side #4	Avg. Length
8	1.6 cm	1.4 cm	2.0 cm	2.4 cm	1.85 cm
9	1.1 cm	1.6 cm	1.8 cm	1.3 cm	1.45 cm
10	1.9 cm	2.4 cm	2.6 cm	2.7 cm	2.40 cm
11	>3.3 cm	3.0 cm	2.8 cm	2.9 cm	>3.00 cm
12	1.6 cm	1.5 cm	1.4 cm	1.5 cm	1.50 cm
13	2.4 cm	2.9 cm	2.8 cm	2.8 cm	2.73 cm

[0042] Review of TABLE 5 indicates that sample no. 11 (50% citric acid/35% aqueous hydrogen peroxide in wood pulp paper) was the most effective at inhibiting the growth of the *E. Coli* bacteria. Sample no. 13 (35% aqueous hydrogen peroxide in kenaf paper) was the next most effective mixture. Hemp paper impregnated with the citric acid/hydrogen peroxide combination evidenced the least biocide activity.

Example Number 4

[0043] A zone of inhibition test of the samples of TABLE 4 in the presence of the Penicillium mold. The experiment was otherwise conducted in the general manner described above in connection with Example Number 2. The results are shown below in TABLE 6:

TABLE 6

Zone of Inhibition Test Using
Wild Strain of *Penicillium* Mold

Sample #	Side #1	Side #2	Side #3	Side #4	Avg. Length
8	1.9 cm	2.0 cm	2.0 cm	1.8 cm	1.92 cm
9	2.3 cm	2.0 cm	2.1 cm	1.9 cm	2.07 cm
10	2.9 cm	2.7 cm	2.8 cm	2.9 cm	2.82 cm
11	2.6 cm	2.3 cm	2.2 cm	2.4 cm	2.37 cm
12	0.0 cm	0.0 cm	0.0 cm	0.0 cm	0.0 cm
13	1.9 cm	2.0 cm	2.1 cm	1.9 cm	1.97 cm

[0044] Review of TABLE 6 indicates that sample no. 9 (50% citric acid/35% aqueous hydrogen peroxide in kenaf paper) was the most effective at inhibiting the growth of the *Penicillium* mold. Sample no. 11 (50% citric acid/35% aqueous hydrogen peroxide in wood paper) was the next most effective combination. Kenaf paper impregnated with citric acid exhibited no biocidal activity.

[0045] The impregnated paper product in accordance with the present invention offers a number of important advantages. One advantage is that the paper can be impregnated with the chemical species directly during the paper-making process. For example, before a large sheet of paper is spooled during manufacture, it can be sprayed with a chemical or immersed in a chemical bath. Similarly, paper pellets can be sprayed or immersed in the chemical immediately after assuming their final physical form.

[0046] Yet another advantage of chemically-impregnated paper in accordance with the present invention is that its relatively cheap cost facilitates replacement when the impregnating chemical material becomes spent or exhausted. This is particularly important in medical treatment applications having a low tolerance for contamination, which require frequent replacement of materials in order to maintain the integrity of the sterile field.

[0047] Another important advantage of the present invention is its environmental compatibility. Examples 1-4 reveal that impregnated kenaf paper has significant biocidal capability. Kenaf is an annual plant having a paper producing potential approximating that of wood, making it an environmentally-friendly alternative paper source. Moreover, the impregnating chemicals acetic acid, citric acid, and limonene are both readily obtained from natural sources. Acetic acid can be obtained by fermentation, citric acid is present in fruits, and limonene is derived from orange peels.

[0048] Although the invention has been described in connection with specific embodiments, it must be understood that the invention as claimed should not be unduly limited to these embodiments. Various other modifications and alterations in the structure and process will be apparent to those skilled in the art without departing from the scope of the present invention.

[0049] For example, while the embodiment of the present invention shown in FIG. 1 describes generating chlorine dioxide from the combination of sodium chlorite and acetic acid, the invention is not limited to these impregnated chemicals. The combination of sodium chlorate and sulfuric acid would also function to generate chlorine dioxide. This is also true for the combination of either sodium chlorate or sodium chlorite and either ferric chlorate or ferric sulfate.

[0050] Moreover, while experimental results have been reported above in conjunction with impregnation of paper with chemicals imparting biocidal activity, paper could be impregnated with a wide variety of other types of chemicals in accordance with the present invention. TABLE 7 provides a partial listing of possible chemicals and chemical combinations suitable for impregnating paper in accordance with the present invention:

TABLE 7

IMPREGNATING CHEMICAL SPECIES	PRODUCT CHEMICAL SPECIES	USES FOR PRODUCT CHEMICAL SPECIES
1)hydrogen peroxide 2)acid (ex. acetic acid)	peracid	biocide
1) sodium chlorite/ sodium chlorate 2)acid (ex. acetic acid)/or metal salt (ex. ferric sulfate)	chlorine dioxide	biocide
phosphoric acid	$(NH_4)_2HPO_4$	odor control (absorption of ammonia)
1) permanganate (ex. potassium permanganate) 2) quarternary ammonium cati on (ex. cetyltrimethylammonium)	$CO_2 + H_2O$	oxidation and removal of organic contaminants from a mixture
potassium hydroxide	$KClO_2 + KCLO_4$	removal of ClO_2
sodium sulfite/or sodium bisulfite	$S_2O_5 = H^+{}_3ClO_3$	removal of ClO_2
manganese dioxide	---	molecular sieve (filtration)

[0051] Examples of the chemicals (or inhibitors of chemicals) usefully impregnated into porous paper products (e.g. sheets of paper or paper pellets) include the following: sodium chlorate; sodium chlorite; ferric chloride; ferric sulfate; peracetic acid; percitric acid; phosphoric acid; sulfuric acid; propionic acid; citric acid; acetic acid; hydrogen peroxide; calcium chloride; magnesium sulfate; potassium chloride; magnesium chloride; sodium bisulfite; sodium metabisulfite; sodium sulfite; limonene; potassium sorbate; potassium hydroxide; amino acids; quarternary ammonium cation (including but not limited to cetyltrimethylammonium chloride); urea; free amines; copper sulfate; zinc sulfate; cobalt sulfate; magnesium sulfate; copper chloride; zinc chloride; cobalt chloride; magnesium chloride; manganese sulfate; manganese chloride; manganese dioxide; sodium selenate; permanganates (including but not limited to potassium permanganate); chlorine; vitamins; lactic acid; benezoic acid; butyric acid; pentenoic acid; succinic acid; glutaric acid; and glycolic acid.

[0052] Given the-multitude of embodiments described above, it is therefore intended that the following claims define the scope of the present invention, and that the compositions and methods within the scope of these claims and their equivalents be covered hereby.